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NO.**

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3	<a href="#">5,478,890 T Olefin polymer composition</a>
4	<a href="#">5,478,884 T Oxyalkylene group-containing polyvinyl alcohol resin composition and process for the production of shaped articles from said composition</a>
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43 5,472,832 T Silver halide photographic element containing antistatic hydrophilic colloid binder layer  
44 5,472,792 T Laminated films  
45 5,472,775 T Elastic materials and articles therefrom  
46 5,472,711 T Agglomerated hydrophilic complexes with multi-phasic release characteristics  
47 5,472,686 T Cosmetic formulations  
48 5,472,627 T Polymeric lubricant additive designed to enhance anti-wear, anti-oxidancy, and dispersancy thereof  
49 5,472,624 T Lubricating compositions containing an amine phosphate with a terminal imide ring  
50 5,472,490 T Pigment composition, printing ink and coating composition

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An intrinsic viscosity [ $\eta$ ] of the olefin polymer according to the invention, as measured in decalin at 135° C., is in the range of 0.05 to 20 dl/g, preferably 0.1 to 15 dl/g, more preferably 0.2 to 13 dl/g.

In the olefin polymer of the invention, the melt tension (MT) and an intrinsic viscosity [ $\eta$ ] also satisfy the following relation.

For example, if the  $\alpha$ -olefin/polyene copolymer (i) and the olefin polymer (ii) both constituting the olefin polymer of the invention are an ethylene/polyene copolymer and polypropylene, respectively, the melt tension and the intrinsic viscosity [ $\eta$ ] in this olefin polymer satisfy the following relation:

generally,  $\log[MT] \geq 3.7 \log [(\eta)] - 1.5$ ;

preferably,  $\log[MT] \geq 3.7 \log [(\eta)] - 1.3$ ;

more preferably,  $\log[MT] \geq 3.7 \log [(\eta)] - 1.1$ ;

most preferably,  $\log[MT] \geq 3.7 \log [(\eta)] - 1.0$ .

If the  $\alpha$ -olefin/polyene copolymer (i) is a copolymer of  $\alpha$ -olefin of 3 or more carbon atoms and polyene and the olefin polymer (ii) is polypropylene in the olefin polymer of the invention, the melt tension and the intrinsic viscosity in this olefin polymer satisfy the following relation:

generally,  $\log[MT] \geq 3.7 \log [(\eta)] - 1.50$ ;

preferably,  $\log[MT] \geq 3.7 \log [(\eta)] - 1.45$ ;

more preferably,  $\log[MT] \geq 3.7 \log [(\eta)] - 1.40$ .

Furthermore, when the olefin polymer of the invention is composed of an ethylene/polyene copolymer (i) and polyethylene (ii) as described above and has a density of about 0.92 g/cm<sup>3</sup> and the intrinsic viscosity [ $\eta$ ] of 1.8 dl/g, the melt tension of this olefin polymer is not less than 2.5 g, preferably not less than 3.5 g, more preferably not less than 4.0 g, much more preferably not less than 4.5 g, most preferably not less than 5.0 g.

The melt tension can be determined in the following manner.

Using a MT measuring machine (produced by Toyo Seiki Seisakusho K.K.), 7 g of a polymer is introduced into a cylinder having an orifice on the bottom and a piston, the cylinder being kept at a melting temperature of the polymer (polyethylene: 190° C.). After 5 minutes, the piston is pushed down at a rate of 10 mm/min. to extrude a molten polymer in the form of strand from the cylinder through the orifice provided on the bottom of the cylinder. The extruded strand is drawn in the form of filament, and wound up at a rate of 25 m/min. by way of a pulley of a load detector. In this stage, a stress applied to the pulley is measured. The obtained value is a melt tension of the polymer.

Next, the transition metal compound catalyst component [A] used for preparing the above-described  $\alpha$ -olefin/polyene copolymer-containing polymer [I] will be described.

The transition metal compound catalyst component [A] used in the invention is a compound containing a transition metal selected from metals in Group III to Group VIII of a periodic table, and preferably is a compound containing at least one transition metal selected from Ti, Zr, Hf, Nb, Ta, Cr and V.

Examples of such transition metal compound catalyst component [A] include a variety of known catalyst components, and concretely are solid titanium catalyst components containing titanium and halogen. In more concrete, one example of the solid titanium catalyst components is a solid titanium catalyst component [A-1] containing titanium, magnesium and halogen, and further containing an electron donor (a) if necessary.

Processes for preparing the solid titanium catalyst component [A-1] are described in detail in the following publications.

That is, the processes are described, for example, in Japanese Patent Publications No. 46(1971)-34092, No. 53(1978)-46799, No. 60(1985)-3323 and No. 63(1988)-54289, Japanese Patent Laid-open Publications No. 1(1989)-261404 and No. 1(1989)-261407, Japanese Patent Publications No. 47(1972)-41676, No. 47(1972)-46269 and No. 48(1973)-19794, Japanese Patent Laid-open Publications No. 60(1985)-262803, No. 59(1984)-147004, No. 59(1984)-149911, No. 1(1989)-201308, No. 61(1986)-151211, No. 53(1978)-58495, No. 53(1978)-87990, No. 59(1984)-205413, No. 58(1983)-206613, No. 58(1983)-125706, No. 63(1988)-68606, No. 63 (1988)-69806, No. 60(1985)-81210, No. 61(1986)-40306; No. 51(1976)-281189, No. 50(1975)-126590 and No. 51(1976)-92885, Japanese Patent Publications No. 57(1982)-45244, No. 57(1982)-26613 and No. 61(1986)-5483, Japanese Patent Laid-open Publication No. 56(1981)-811, Japanese Patent Publications No. 60(1985)-37804 and No. 59(1984)-50246, Japanese Patent Laid-open Publications No. 58(1983)-83006, No. 48(1973)-16986, No. 49(1974)-65999 and No. 49(1974)-86482, Japanese Patent Publications No. 56(1981)-39767 and No. 56(1981)-32322, and Japanese Patent Laid-open Publications No. 55(1980)-29591, No. 53(1978)-146292, No. 57(1982)-63310, No. 57(1982)-63311, No. 57(1982)-63312, No. 62(1987)-273206, No. 63(1988)-69804, No. 61(1986)-21109, No. 63(1988)-264607, No. 60(1985)-23404, No. 60(1985)-44507, No. 60(1985)-158204, No. 61(1986)-55104, No. 2(1990)-28201, No. 58(1983)-196210, No. 64(1989)-54005, No. 59(1984)-149905, No. 61(1986)-145206, No. 63(1988)-302, No. 63(1988)-225605, No. 64(1989)-69610, No. 1(1989)-168707, No. 62(1987)-104810, No. 62(1987)-104811, No. 62(1987)-104812 and No. 62(1987)-104813.

The solid titanium catalyst component [A-1] can be prepared by using for example a titanium compound, a magnesium compound and if desired an electron donor (a), and bringing them into contact with each other.

Examples of the titanium compounds employable for preparing the solid titanium catalyst component [A-1] include tetravalent titanium compounds and trivalent titanium compounds.

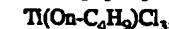
As the tetravalent titanium compounds, there can be mentioned compounds represented by the following formula:



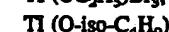
wherein R is a hydrocarbon group, X is a halogen atom, and g is a number satisfying the condition of  $0 \leq g \leq 4$ .

Concrete examples of such compounds are described below.

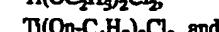
Titanium tetrahalides such as  $TiCl_4$ ,  $TiBr_4$  and  $TiI_4$ . Alkoxytitanium trihalides such as:



$Ti(OC_2H_5)_2Br_3$  and



Dialkoxytitanium dihalides such as:



Trialkoxytitanium monohalides such as:



10. The olefin polymer composition of claim 1 or claim 2 wherein the  $\alpha$ -olefin/polyene copolymer (i) is selected from the group consisting of copolymers of ethylene and 1,7-octadiene, ethylene and 1,9-decadiene, ethylene and 1,13-tetradecadiene, ethylene and 1,5,9-decatriene, propylene and 1,7-octadiene, propylene and 1,9-decadiene, propylene and 1,13-tetradecadiene, propylene and 1,5,9-decatriene, butene and 1,9-decadiene, butene and 1,5,9-decatriene, 4-methyl-1-pentene and 1,9-decadiene, 3-methyl-1-butene and 1,9-decadiene, 1-eicosene and 1,9-decadiene, propylene and 1,4-divinylcyclohexane and butene and 1,4-divinylcyclohexane, said  $\alpha$ -olefin/polyolefin copolymer having a melt flow rate of no more than 0.1 dg/min.

11. The olefin polymer composition of claim 1 or claim 2 which contains the  $\alpha$ -olefin/polyene copolymer (i) in an amount of from 0.008 to 10% by weight and the olefin polymer (ii) in an amount of from 99.992 to 90% by weight.

12. The olefin polymer composition of claim 11 wherein the  $\alpha$ -olefin/polyene copolymer (i) contains constituent units derived from the polyene in an amount of from 0.01 to 20% by mole and constituent units derived from the  $\alpha$ -olefin in an amount of from 99.99 to 80% by mole.

13. The olefin polymer composition of claim 1 wherein the  $\alpha$ -olefin of copolymer (i) is ethylene and the olefin polymer (ii) is polypropylene, and wherein the melt tension and the melt flow rate satisfy the following relation:

$$\log(MT) \geq -0.8 \log(MFR) + 0.8.$$

14. The olefin polymer composition of claim 1 wherein the  $\alpha$ -olefin of the copolymer (i) is an  $\omega$ -olefin of three or more carbon atoms and wherein the olefin polymer (ii) is polypropylene, and wherein the melt tension and the melt flow rate satisfy the following relation:

$$\log(MT) \geq -0.8 \log(MFR) + 0.40.$$

15. The olefin polymer composition according to claim 13 having a melt flow rate (MFR) of from about 0.5 g/10 min to about 6 g/10 min, and a melt tension (MT) of from about 2.2 g to about 32 g.

16. The polymer composition according to claim 13 having an intrinsic viscosity ( $\eta$ ) in the range of 0.1 to 15 dl/g, and wherein the melt tension and intrinsic viscosity ( $\eta$ ) satisfy the following relation:

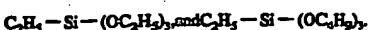
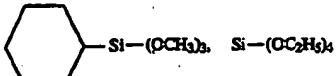
$$\log(MT) \geq 3.7 \log(\eta) - 1.3.$$

17. The olefin polymer composition according to claim 14 wherein the intrinsic viscosity, as measured in decalin at 135°, is in the range of from 0.1 to 15 dl/g, and wherein the melt tension MT and the intrinsic viscosity ( $\eta$ ) satisfy the following relation:

$$\log(MT) \geq 3.7 \log(\eta) - 1.45.$$

\* \* \* \* \*

wherein R<sup>4</sup> is a cycloalkyl group or an alkyl group and R<sup>5</sup> is a cycloalkyl group. Specific examples of such compounds are shown below.



The silicon compound (2) is used in such an amount as to give a molar ratio of the silicon compound (2) to titanium in the component (a) which is usually in the range of 1-500, 15 and is preferably in the range of 5-200.

In the second step, an ethylene-propylene block copolymer containing a highly stereospecific and highly crystalline copolymer portion is obtained by copolymerizing ethylene and propylene to form an ethylene-propylene copolymer portion having an ethylene content of at least 20% by weight. The copolymerization should be conducted such that the ethylene-propylene copolymer portion is formed in an amount of 5-50% by weight, preferably 10-40% by weight, of the total polymerization amount of the ethylene-propylene block copolymer. 25

In the second step, the polymerization temperature is usually 20°-200° C., and is preferably 50°-90° C., and the polymerization pressure is usually from atmospheric pressure to 100 kg/cm<sup>2</sup>G, and is preferably 2-50 kg/cm<sup>2</sup>G.

The reaction of the second step may also be conducted in two or more stages as in the first step. In such a case, the polymerization conditions in respective stages may be different from one another. The ethylene-propylene copolymer formed in the second step can be controlled by using hydrogen so as to have an intrinsic viscosity [η] (determined in decalin at 135° C.) which is usually 0.5-8.0, preferably 0.5-6.0, and more preferably 1.0-4.0.

The present invention can be applied to various processes, for example, gas-phase polymerization, slurry polymerization, etc. When a slurry polymerization is adopted, it can be conducted by using an inert hydrocarbon solvent such as hexane, heptane, etc.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is described in more detail below with reference to Examples and Comparative Examples, but the Examples should not be construed as limiting the scope of the present invention.

The properties of polymer shown in Examples were determined in the following manner.

##### (1) MI

This was determined in accordance with the method specified in JIS K 6758, at a measuring temperature of 230° C. and a load of 2.16 kg/cm<sup>2</sup>.

##### (2) FE (fish eye)

A 100 cm<sup>2</sup> piece was cut out from a T-die extrusion film of 30 µm thickness, and the number of fish eyes having a diameter of 200 µm or more was determined by using a peak scale of 10 magnifications.

Polymers with a small number of fish eyes give a good appearance in molding.

##### (3) Tensile property

In accordance with the method specified in ASTM D 638, tensile yield strength and tensile elongation were determined

with a test piece of 3.2 mm thickness at a measuring temperature of 23° C.

##### (4) Flexural property

In accordance with the method specified in JIS K 7203, flexural modulus of elasticity was determined with a test piece of 3.2 mm thickness under conditions of a span length of 50 mm, loading velocity of 1.5 mm/min and measuring temperature of 23° C.

##### (5) Izod impact strength

In accordance with the method specified in JIS K 7110, impact strength with notch was determined with a test piece of 3.2 mm thickness at measuring temperatures of 23° C. and -20° C.

##### (6) Falling weight impact strength

Resin was injection-molded into a sheet of 1 mm thickness, and a disk having a diameter of 66 mm was punched out from the sheet and used as a test piece. The test piece was conditioned at 23° C. and 50% RH for at least 40 hours, then kept at the measuring temperature (0° C. or -20° C.) for at least 2 hours, and thereafter the fracture strength was determined with a dupont impact tester using weights of 0.10-3 kg.

##### (7) Ethylene content

Ethylene content was determined from the infrared absorption spectrum.

#### REFERENTIAL EXAMPLE

##### (A) Synthesis of organomagnesium compound

A 1-l flask fitted with a stirrer, reflux condenser, dropping funnel and thermometer was flushed with argon gas, and 32.0 g of magnesium turnings for Grignard reagent were placed in the flask. Into the dropping funnel were charged 120 g of butyl chloride and 500 ml of dibutyl ether, and about 30 ml of the resulting mixture was added dropwise onto the magnesium in the flask to initiate the reaction. After initiation of the reaction, the dropwise addition was continued at 50° C. over a period of 4 hours. After completion of the addition, the reaction was continued at 60° C. for additional 1 hour. Thereafter the reaction liquid was cooled to room temperature and then filtered to remove solid materials.

The concentration of butylmagnesium chloride in dibutyl ether was determined by hydrolyzing the filtrate with 1-N sulfuric acid, followed by back titration with a 1-N aqueous sodium hydroxide solution using phenolphthalein as an indicator. The concentration was found to be 2.1 mol/l.

##### (B) Synthesis of solid product

A 500-ml flask fitted with a stirrer and a dropping funnel was flushed with argon gas, and 240 ml of hexane, 5.4 g (15.8 mmols) of tetrabutoxytitanium and 61.4 g (295 mmols) of tetraethoxysilane were charged thereinto to form a uniform solution. Then, 150 ml of the organomagnesium compound synthesized in (A) above was gradually added dropwise from the dropping funnel over a period of 4 hours while keeping the temperature in the flask at 5° C. After completion of the dropwise addition, the reaction mixture was stirred for further 1 hour at room temperature and then separated at room temperature into solid and liquid. The solid was washed 3 times with 240 ml of hexane, and then dried to obtain 45.0 g of a brown solid product.

The solid product contained 1.7% by weight of titanium atoms, 33.8% by weight of ethoxy groups and 2.9% by weight of butoxy groups.

The wide angle X-ray diffraction pattern of the solid product obtained by using Cu-Kα line showed utterly no distinct diffraction peak, revealing that the product was of an amorphous structure.



wherein  $R^{10}$  is a hydrocarbon group having 1 to 12 carbon atoms, an alkoxy group having 1 to 12 carbon atoms, an aryloxy group having 6 to 20 carbon atoms, a hydroxyl group, a halogen or hydrogen.

$R^{10}$  in the formula (VII) and  $R^9$  in the formula (VI) are groups different from each other.

When said compound (B-2) contains the oxyaluminum unit (ii), an organoaluminum oxy compound containing the alkyloxyaluminum unit (i) in an amount of at least 30 mol %, preferably at least 50 mol %, especially preferably at least 70 mol % is desirous.

The above organoaluminum oxy compound (B) is usually commercially available as a toluene solution.

The organoaluminum oxy compound (B) used in this invention may contain a small amount of an organic compound component of a metal other than aluminum.

The organoaluminum oxy compound (B) can also be used as being supported on the above carrier compound.

The above catalyst for polymerization is formed from the aforesaid metallocene compound (A) and organoaluminum compound (B), and may further contain, together with these compounds (A) and (B), the organoaluminum compound (C) as required. As the organoaluminum compound (C), an organoaluminum compound represented by the formula (VIII) can be mentioned, for example.



(VIII)

30

wherein  $R^{11}$  is a hydrocarbon group having 1 to 12 carbon atoms, X is a halogen or hydrogen atom, and n is an integer of 1 to 3.

The hydrocarbon group having 1 to 12 carbon atoms includes an alkyl group, a cycloalkyl group and an aryl group. Specific examples of the hydrocarbon group include methyl, ethyl, n-propyl, isopropyl, isobutyl, pentyl, hexyl, octyl, cyclopentyl, cyclohexyl, phenyl and tolyl groups.

Specific examples of such organoaluminum compound include:

trialkylaluminums such as trimethylaluminum, triethylaluminum, triisopropylaluminum, triisobutylaluminum, trioctylaluminum and tri-2-ethylhexylaluminum,

alkenylaluminums such as isoprenylaluminum,

dialkylaluminum halides such as dimethylaluminum chloride, diethylaluminum chloride, diisopropylaluminum chloride, diisobutylaluminum chloride and dimethylaluminum bromide,

alkylaluminum sesquihalides such as methylaluminum sesquichloride, ethylaluminum sesquichloride, isopropylaluminum sesquichloride, butylaluminum sesquichloride and ethylaluminum sesquibromide,

alkylaluminum dihalides such as methylaluminum dichloride, ethylaluminum dichloride, isopropylaluminum dichloride and ethylaluminum dibromide, and

alkylaluminum hydrides such as diethylaluminum hydride and diisobutylaluminum hydride.

As the organoaluminum compound (C), a compound represented by the formula (IX) can also be used.



(IX)

wherein  $R^{11}$  is the same as defined in the above formula (VIII); Y is  $-OR^{12}$ ,  $-OSIR^{13}_3$ ,  $-OAlR^{14}_2$ ,  $-NR^{15}_2$ ,  $-SiR^{16}_3$  or  $-N(R^{17})AlR^{18}_2$  in which  $R^{12}$ ,  $R^{13}$ ,  $R^{14}$  and  $R^{18}$

(VII)

are each a methyl, ethyl, isopropyl, isobutyl, cyclohexyl or phenyl group,  $R^{15}$  is hydrogen or a methyl, ethyl, isopropyl, phenyl or trimethylsilyl group, and  $R^{16}$  and  $R^{17}$  are each a methyl or ethyl group; and n is an integer of 1 to 2.

Specific examples of such organoaluminum compound include:

(i) compounds represented by the formula  $R^{11}_n Al(OR^{12})_{3-n}$ , such as dimethylaluminum methoxide, diethylaluminum ethoxide and diisobutylaluminum methoxide,

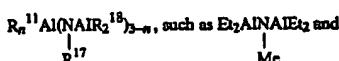
(ii) compounds represented by the formula  $R^{11}_n Al(OSIR^{13}_3)_{3-n}$ , such as  $Et_2Al(OSiMe_3)$ ,  $(iso-Bu)_2Al(OSiMe_3)$  and  $(iso-Bu)_2Al(OSiEt_3)$ ,

(iii) compounds represented by the formula  $R^{11}_n Al(OAl^{14})_{3-n}$ , such as  $Et_2AlOAlEt_2$  and  $(iso-Bu)_2AlOAl(iso-Bu)_2$ ,

(iv) compounds represented by the formula  $R^{11}_n Al(NR^{15})_{2-n}$ , such as  $Me_2AlNEt_2$ ,  $Et_2AlNHMe$ ,  $Me_2AlNHEt$ ,  $Et_2AlN(SiMe_3)_2$  and  $(iso-Bu)_2AlN(SiMe_3)_2$ ,

(v) compounds represented by the formula  $R^{11}_n Al(SiR^{16})_{3-n}$ , such as  $(iso-Bu)_2AlSiMe_3$ , and

(vi) compounds represented by the formula  $R^{11}_n Al(NAIR^{18})_{2-n}$ , such as  $Et_2AlNAIEt_2$  and



In this invention, among the above organoaluminum compounds (C), the trialkylaluminum is preferable, and triisobutylaluminum is especially preferable. These organoaluminum compounds (C) can be used either singly or in combination.

The catalyst for polymerization used in this invention is formed of the aforesaid catalyst components (A), (B) and optionally (C). At this time, the metallocene compound (A) is used in an amount of usually about 0.00005 to 0.1 mmol, preferably about 0.0001 to 0.05 mmol, calculated as a transition metal atom, per liter of the polymerization volume, and the organoaluminum oxy compound (B) is used such that the amount of the aluminum atom in the organoaluminum oxy compound (B) is usually about 1 to 10,000 mols, preferably 10 to 5,000 mols, per mol of the transition metal atom of the metallocene compound (B). Further, when the organoaluminum compound (C) is used, the amount of said compound (C) is usually about 0 to 200 mols, preferably about 0 to 100 mols, per mol of the aluminum atom of the organoaluminum oxy compound (B).

The molecular weight of the ethylene/ $\alpha$ -olefin copolymer rubber can be defined by the Mooney viscosity of the chlorinated ethylene/ $\alpha$ -olefin copolymer rubber. An ethylene/ $\alpha$ -olefin copolymer rubber before the chlorination which has an intrinsic viscosity  $[\eta]$ , measured at 135° C. in decalin, of 0.5 to 6.0 is preferably used. The chlorinated ethylene/ $\alpha$ -olefin copolymer rubber is obtained by chlorinating the above obtained ethylene/ $\alpha$ -olefin copolymer rubber.

The ethylene/ $\alpha$ -olefin copolymer rubber can be chlorinated by, for example, dissolving the copolymer rubber in a solvent and bringing the solution into contact with molecular chlorine in the presence of light or an organic peroxide as a catalyst. In the reaction, a solvent can be used. Examples of

## Preparation of a Prepolymerized Catalyst

The procedure for preparing the prepolymerized catalyst in Preparation Example 1 was repeated except for using the catalyst component prepared above, to obtain a prepolymerized catalyst.

## Polymerization

The procedure for the polymerization in Example 4 was repeated except for using the prepolymerized catalyst prepared above, to obtain an ethylene/1-hexene copolymer different in MFR and density from the copolymer of Example 4. The copolymer thus obtained had MFR of 1.2 g/10 min, a density of 0.920 g/cm<sup>3</sup> and a decane-soluble portion quantity at 23° C. of 0.52% by weight.

The ethylene/1-hexene copolymer was subjected to inflation in the same manner as described in Example 1 to form a film having a thickness of 30 µm.

Melt properties and other properties of the ethylene/1-hexene copolymer and physical properties of the film formed from the copolymer are set forth in Table 4.

As is evident from Table 4, an inflation film excellent in moldability, optical characteristics and mechanical strength was obtained from the copolymer.

## Comparative Example 5

Copolymerization of ethylene with 1-hexene was carried out by the use of one fluidized bed gas phase polymerizer of continuous type. The catalyst used herein was the same as that used in Example 6.

The ethylene/1-hexene copolymer obtained above had MFR of 1.2 g/10 min and a density of 0.919 g/cm<sup>3</sup>.

The ethylene/1-hexene copolymer was subjected to inflation in the same manner as described in Example 1 to form a film having a thickness of 30 µm.

Melt properties and other properties of the ethylene/1-hexene copolymer and physical properties of the film formed from the copolymer are set forth in Table 4.

As is evident from Table 4, the ethylene/1-hexene copolymer obtained in Example 6 was superior in the flow index (FI) within high-shear region to that of Comparative Example 5, and the inflation film obtained in Example 6 was superior in the film impact to that of Comparative example 5, although the copolymer of Example 6 was almost the same as the copolymer of Comparative Example 5 in the MFR and the density.

TABLE 4

Comonomer	Cata-		First Stage				
	Kind	Amount mol. %	lyst <sup>*1</sup> by mol	MFR g/10- min	[η] dl/g	Mw/ Mn	Densi- ty g/cm <sup>3</sup>
Ex. 4	1-hexene	—	9/1	0.50	2.09	2.6	0.912
Comp.	1-	2.9	9/1	—	—	—	—
Ex. 3	hexene	—	8/2	0.45	2.10	2.8	0.911
Ex. 5	1-hexene	—	8/2	—	—	—	—
Comp.	1-	2.9	8/2	—	—	—	—
Ex. 4	hexene	—	7/3	0.38	2.21	3.0	0.909
Ex. 6	1-hexene	—	7/3	—	—	—	—
Comp.	1-	3.3	7/3	—	—	—	—
Ex. 5	hexene	—	—	—	—	—	—

TABLE 4-continued

	n-Decane Soluble Portion wt. %	Tm °C.	MT g	First Stage			MT Mw/Mn	FI s <sup>-1</sup>
				*2	FI s <sup>-1</sup>	*3		
Ex. 4	0.55	99.6	6.4	3.9	32	75	2.46	0
Comp.	—	—	—	—	—	—	—	—
Ex. 3	0.48	101.0	6.0	4.3	53	68	2.14	0.53
Comp.	—	—	—	—	—	—	—	—
Ex. 4	0.56	93.5	7.2	5.0	49	57	2.40	0.87
Comp.	—	13	—	—	—	—	—	—
Ex. 5	—	—	—	—	—	—	—	—

	MFR g/10- min	Densi- ty g/cm <sup>3</sup>	n-Decane		Tm °C.	MT g	FI s <sup>-1</sup>
			Soluble Portion wt. %				
Ex. 4	1.5	0.922	0.51	—	—	3.1	176
Comp.	1.5	0.922	—	—	114.4	3.1	105
Ex. 3	—	—	—	—	—	—	—
Ex. 5	2.2	0.923	0.46	—	—	2.0	353
Comp.	2.1	0.923	—	—	114.5	2.1	212
Ex. 4	—	—	—	—	—	—	—
Ex. 6	1.2	0.920	0.52	—	—	4.5	213
Comp.	—	—	—	—	—	—	—
Ex. 5	1.2	0.919	0.57	—	114.2	4.5	94

	Physical Properties of Film				
	Haze %	Gloss %	Impact Strength kg · cm/cm	Moldabil- ity	*6
Ex. 4	8.0	69	NB <sup>*5</sup>	AA	
Comp. Ex. 3	4.4	89	3,950	AA	
Ex. 5	8.4	63	6,880	BB	
Comp. Ex. 4	4.6	85	3,270	BB	
Ex. 6	8.8	57	NB <sup>*5</sup>	AA	
Comp. Ex. 5	6.2	61	7,320	AA	

\*1 Zirconium compound in the catalyst component

I: bis(1,3-n-butylmethylecyclopentadienyl)zirconium dichloride

II: bis(1,3-dimethylcyclopentadienyl)zirconium dichloride

\*2 value of 2.2 × MFR-0.84

\*3 value of 150 × MFR

\*4 value of 0.03 × FI/MFR-3.0 (In the case of less than 0, the value is taken as 0.)

\*5 NB: not broken (film impact > 8,500 kg · cm/cm)

\*6 Moldability

AA: MT ≥ 3 g

BB: 3 g > MT ≥ 2 g

CC: 2 g > MT

What is claimed is:

1. An ethylene/α-olefin copolymer composition comprising:

[A1] an ethylene/α-olefin copolymer in an amount of 20 to 90% by weight, which is obtained by copolymerizing ethylene with an α-olefin of 3 to 20 carbon atoms in the presence of a catalyst for olefin polymerization comprising (a) an organoaluminum oxy-compound and (b) at least two kinds of compounds of Group IV transition metals of the periodic table containing a ligand having a cyclopentadienyl skeleton, and which has such properties that:

(A-i) the density is in the range of 0.850 to 0.980 g/cm<sup>3</sup>, and

(A-ii) the intrinsic viscosity [η] as measured in decalin at 135° C. is in the range of 0.4 to 8 dl/g; and

(A-iii) the melt tension (MT(g)) at 190° C. and the melt flow rate (MFR) satisfy the relation

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above ranges, the activity may be decreased.

The olefin polymerization catalysts of the present invention, prepared as above, may have an average particle size of usually from 2 to 200  $\mu\text{m}$ , preferably from 10 to 150  $\mu\text{m}$ , more preferably from 20 to 100  $\mu\text{m}$ ; and a specific surface area of usually from 20 to 1,000  $\text{m}^2/\text{g}$ , preferably from 50 to 500  $\text{m}^2/\text{g}$ . If the average particle size is less than 2  $\mu\text{m}$ , small particles in the resultant polymers may increase. If the average particle size is more than 200  $\mu\text{m}$ , large particles in the resultant polymers may increase. If the specific surface area is less than 20  $\text{m}^2/\text{g}$ , the activity may be decreased. If the specific surface area is more than 1000  $\text{m}^2/\text{g}$ , the bulk density of the resultant polymers may be decreased.

Further, in the catalysts of the present invention, the amount of the transition metal contained in 100 g of the carrier may usually be from 0.05 to 10 g, preferably from 0.1 to 2 g. If the amount of the transition metal is outside of the above ranges, the activity may be decreased.

As mentioned above, the use of Carrier (D) may result in the resultant polymers having high bulk density and excellent particle size distribution, which are industrially useful.

##### 5. Production Process of Polymers:

According to the process for producing the polymers of the present invention, homopolymerization of an olefin alone, or copolymerization of an olefin and ethylene, the other olefin or the other unsaturated compounds is carried out in the presence of the above-mentioned polymerization catalyst.

In this case, the kind of olefins are not particularly limited. But, alpha-olefins having 2 to 20 carbon atoms are preferable. More specifically, suitable alpha-olefins include, for example, ethylene, propylene, 1-butene, 3-methyl-1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, styrene, p-methylstyrene, p-chlorostyrene, p-t-butylstyrene, p-phenylstyrene, p-methylsilylstyrene and p-trimethylsilylstyrene.

In the present invention, when two or more of alpha-olefins are copolymerized, any combination of the above monomers can be used. In the case of copolymerizing ethylene and an alpha-olefin having 3 to 10 carbon atoms, a molar ratio of ethylene to the other alpha-olefins may be usually 99.9:0.1 to 60.0:40.0, preferably 99.5:0.5 to 75.0:25.0.

In the present invention, in addition to the above alpha-olefins, it is possible to polymerize, or copolymerize with the other unsaturated compounds such as chain diolefins such as butadiene, isoprene and 1,5-hexadiene, cyclic olefins such as norbornene and 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, cyclic diolefins such as norbornadiene and ethylidene norbornene, unsaturated esters such as ethylacrylate and methylmethacrylate, and lactones such as beta-propiolactone, beta-butyrolactone and gamma-butyrolactone.

In general, the amount of the other unsaturated compounds may be not greater than 20 mole percent based on the amount of the olefin. In this case, one or more olefins may preferably be used.

Polymerization methods are not particularly limited to, but include slurry polymerization, gas phase polymerization, bulk polymerization, solution polymerization and suspension polymerization. Slurry polymerization and gas phase polymerization are particularly preferred.

As for polymerization conditions, the polymerization

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temperature may range from -100° to 250° C., preferably from -50° to 200° C., more preferably from 0° to 130° C. Further, the catalyst is preferably used in an amount to provide a starting monomer/Component (A) molar ratio or a starting monomer/Component (B) molar ratio of from 1 to 10<sup>8</sup>, preferably from 100 to 10<sup>3</sup>. The polymerization time may usually range from 5 minutes to 10 hours. The reaction pressure may range from normal pressure to 100 Kg/cm<sup>2</sup>G, preferably from normal pressure to 30 Kg/cm<sup>2</sup>G.

The molecular weight of the resultant polymer can be controlled by appropriately selecting the amount of each catalyst component and polymerization temperature, or by a polymerization reaction in the presence of hydrogen.

In the case of using polymerization solvents, suitable solvents include aromatic hydrocarbons such as benzene, toluene, xylene and ethylbenzene; alicyclic hydrocarbons such as cyclopentane, cyclohexane and methylcyclohexane; aliphatic hydrocarbons such as pentane, hexane, heptane and octane; and halogenated hydrocarbons such as chloroform and dichloromethane. These solvents can be used alone or in combination. Monomers such as alpha-olefins can also be used as solvent. In addition, the polymerization can be carried out in the absence of a solvent.

In the polymerization process of the present invention, pre-polymerization can be carried out in the presence of the catalyst according to the present invention.

The pre-polymerization can be carried out by any known methods such as a method of bringing a small amount of olefins into contact with the solid catalyst components.

The olefins which can be used in the pre-polymerization are not particularly limited to, but include those olefins mentioned above such as ethylene, C<sub>3-20</sub> alpha-olefins or mixtures thereof. It is preferable to use, for the pre-polymerization, the same olefin used in the subsequent polymerization.

Further, the pre-polymerization temperature may usually range from -20° to 100° C., preferably from -10° to 70° C., more preferably from 0° to 50° C.

In the pre-polymerization, inert hydrocarbons, aliphatic hydrocarbons, aromatic hydrocarbons, monomers or the like, can be used as a solvent. Of these, aliphatic hydrocarbons are particularly preferable. In addition, the pre-polymerization can be carried out in the absence of a solvent.

In the pre-polymerization, it is preferable to adjust conditions so that the intrinsic viscosity of the pre-polymer (measured at 135° C. in decalin) ranges at least 0.2 dL/g, preferably at least 0.5 dL/g, and that the yield of the pre-polymer ranges from 1 to 10,000 g, preferably from 10 to 1,000 g per 1 millimoles of the transition metal component in the catalyst used.

As mentioned above, the polymerization catalysts according to the present invention show high activities, and the resultant olefin homopolymer or copolymer of olefins produced using the catalysts, will have high molecular weight, and narrow comonomer distribution. Also, the molecular weight and the molecular weight distribution can be controlled. Further, the polymers or copolymers having excellent properties can be effectively produced without using a great amount of an organometallic compound.

##### EXAMPLES

The present invention will be described in more detail with reference to the following Examples and Comparative Examples, which are not used to limit the present invention.

In addition, in the Examples and the Comparative

## RESIN COMPOSITION HAVING EXCELLENT PAINT COATABILITY

This is a divisional of parent application Ser. No. 08/329, 136, filed Oct. 25, 1994, which is a continuation of grandparent application Ser. No. 08/042,653, filed April 2, 1993, now abandoned. Priority is claimed from Jul. 4, 1992 based on Japanese Patent Application No. 4-170149. The priority document was filed in grandparent Application No. 08/042, 653.

### BACKGROUND OF THE INVENTION

The present invention relates to a resin composition for exterior automotive parts, and more particularly to a resin composition having excellent paint coatability and moldability, a good balance of impact resistance, ductility, mechanical strength, thermal deformation resistance, brittle temperature, hardness, etc., small molding shrinkage and linear expansion coefficient, and a high paint coating peeling resistance in high-temperature, high-pressure washing.

Since polypropylene is light and has excellent mechanical strength, it is used in various applications. However, since it is poor in impact resistance, its copolymers such as propylene-ethylene block copolymers are used. Also, proposals have been made to provide a resin composition comprising a propylene-ethylene block copolymer, an ethylene- $\alpha$ -olefin copolymer elastomer and an inorganic filler such as talc.

Japanese Patent Laid-Open No. 61-12742 discloses a resin composition comprising (a) 62-57 weight % of a propylene-ethylene block copolymer having an ethylene content of 2-3 weight % and a melt flow rate of 40-45 g/10 minutes, (b) 26-28 weight % of an ethylene-propylene copolymer elastomer having an ethylene content of 70-80 weight % and a Mooney viscosity ML<sub>1.4</sub> (100°C.) of 55-58, (c) 2-3 weight % of a high-density polyethylene having a density of 0.955-0.960 g/cm<sup>3</sup> and a melt flow rate of 18-22 g/10 minutes, and (d) 10-12 weight % of talc having an average size of 1.8-2.2  $\mu$ m and a specific surface area of 36000-42000 cm<sup>2</sup>/g, the resin composition having a melt flow rate of 13-18 g/10 minutes, a density of 0.950-0.980 g/cm<sup>3</sup>, a flexural modulus of 11500-14000 kg/cm<sup>2</sup>, a linear expansion coefficient of 7x10<sup>-5</sup>-10x10<sup>-5</sup> cm/cm°C. in a temperature range between 20° C. and 80° C., and a surface gloss (measured by a 60°-60° method according to JIS Z8741) of 55% or more.

Japanese Patent Laid-Open No. 1-149845 discloses a resin composition comprising (a) 59-74 weight % of a propylene-ethylene block copolymer containing 5-12 weight % of a boiling p-xylene-soluble component having an ethylene content of 20-60 weight %, and having an ethylene content of 1-7 weight % and a melt flow rate of 15-50 g/10 minutes, (b) 35-20 weight % of an ethylene-propylene copolymer elastomer having a propylene content of 20-60 weight % and a Mooney viscosity ML<sub>1.4</sub> (100°C.) of 100-150, and (c) 3-6 weight % of talc having a specific surface area of 30000 cm<sup>2</sup>/g or more and an average size of 0.5-2.0  $\mu$ m.

However, both resin compositions of Japanese Patent Laid-Open Nos. 61-12742 and 1-149845 are susceptible to thermal deformation, and bumpers made of such resin compositions would be easily deformed due to the difference in a linear expansion coefficient between the resin compositions and the automotive body parts in a high-temperature environment, resulting in the deterioration of automotive body appearance. Also, since beautiful coatings are recently

formed on bumpers, etc., the resin compositions for bumpers, etc. should have good paint coatability in order to provide the automotive bodies with good appearance.

In the above-described resin compositions comprising the propylene-ethylene block copolymer, the ethylene-propylene copolymer elastomer (or high-density polyethylene) and talc, their flowability is controlled for various applications by adjusting ethylene/propylene ratios and molecular weights, etc. in the propylene-ethylene block copolymer and the ethylene-propylene copolymer elastomer. However, the control of such parameters fails to provide resin compositions having well balanced properties such as paint coatability, moldability, rigidity, ductility, thermal deformation resistance, brittle temperature, hardness, etc. on levels suitable for exterior automotive parts.

As a polypropylene resin composition for automotive bumpers having an improved paint coatability, Japanese Patent Laid-Open No. 57-55952 discloses a polypropylene resin composition comprising 55-65 weight % of a crystalline propylene-ethylene block copolymer containing 5-10 weight % of ethylene, a propylene component, 97 weight % or more of which is insoluble in boiling n-heptane, and a component soluble in p-xylene at a room temperature having an intrinsic viscosity (in decalin at 135° C.) of 3-4 and a melt flow rate of 2-10; 30-35 weight % of an amorphous ethylene-propylene copolymer elastomer having an intrinsic viscosity (in decalin at 135° C.) of 2.0-3.5 and a Mooney viscosity ML<sub>1.4</sub> (100°C.) of 40-100; and 5-15 weight % of talc having an average size of 0.5-5  $\mu$ m. This resin composition shows an improved resistance to peeling of coatings formed thereon, but it fails to show a sufficient peeling resistance of the coatings in washing under severe conditions such as high temperature and/or high pressure.

### OBJECT AND SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a resin composition for exterior automotive parts having excellent paint coatability and moldability, and well balanced impact resistance, ductility, mechanical strength, thermal deformation resistance, brittle temperature and hardness while showing small molding shrinkage and linear expansion coefficient.

Another object of the present invention is to provide a resin composition for exterior automotive parts further having good peeling resistance of coatings under severe conditions such as high-temperature, high-pressure washing.

As a result of intense research in view of the above objects, the inventors have found that by blending a propylene-ethylene block copolymer produced by a multi-stage polymerization, an ethylene- $\alpha$ -olefin copolymer elastomer and an inorganic filler, and by controlling the content of propylene-ethylene random copolymer portion in the resulting resin composition and various parameters of the components, the resulting resin composition shows well balanced impact resistance, ductility, mechanical strength, thermal deformation resistance, brittle temperature and hardness.

With respect to the peeling resistance of a coating formed on a resin molding substrate under severe conditions such as high-temperature, high-pressure washing, the inventors have also found that the peeling resistance is usually determined by a Young's modulus of the coating, the strength of a substrate and an adhesion strength between the coating and the substrate, and that if the adhesion strength between the coating and the substrate is large enough, the peeling resis-

Molecular Weight Polymer". (General Information and Applications) (1989). Due to the unusually long chain length, VHMW and UHMW polyethylene resins exhibit a melt index of zero grams/10 minutes under standard test conditions. Consequently VHMW and UHMW polyethylene resins are not readily processable in the usual extrusion or injection molding equipment. In fact, Miller, referred to above, reports that efforts at screw extrusion of ultra high molecular weight polyethylene have resulted in polymer degradation or equipment damage. As a consequence, VHMW and UHMW polyethylene resins are usually extruded into sheet profiles via a ram extrusion process, or molded into specific shapes by cold forging, sintering or compression molding.

Generally, also, the high molecular weight polyethylenes which are utilized in the present invention are those wherein the intrinsic viscosity, as measured at 135° C. in decahydronaphthalene (also called decalin), is greater than 5 and up to about 30 and, preferably, is between about 14 and 30, with the intrinsic viscosity of the VHMW being within the range of about 14 to about 20, and the intrinsic viscosity of UHMW being within the range of about 20 to 30, or higher.

The amount of the high molecular weight polyethylene which can be incorporated into the presently claimed compositions varies. Applicants have found that in compositions comprised of polyphenylene ether resin/high impact polystyrene resin blends, no evidence of delamination in injected molten parts was seen in compositions containing up to the maximum amount of VHMW or UHMW polyethylene resin included into such compositions. Also, the use of VHMW or UHMW polyethylene resins in amounts of as low as about 0.75 phr begins to show anti-dripping effects in the resin compositions tested while, generally, the use of high molecular weight (HMW), VHMW and UHMW polyethylene resins in amounts of between 3 phr to about 6 phr in compositions comprised of flame retardant polyphenylene ether resin/polystyrene resin blends substantially, and often completely, eliminates dripping in the UL 94 5 V flammability testing of  $\frac{1}{16}$  inch injection molded bars.

The amount of polyphenylene ether resin can vary substantially as well. The polyphenylene ether resin can be used per se as the only polymeric resin in the compositions, or can be used in combination with a vinyl aromatic resin. When used in combination with a vinyl aromatic resin, all miscible ratios (i.e. from 1% to 99% by weight of polyphenylene ether resin and from 99% to 1% by weight of vinyl aromatic resin) are suitable for use in the present invention. Preferably, in such combinations of resins, the amount of polyphenylene ether resin will be greater than about 20%, more preferably greater than about 30%, and most preferably greater than about 50% by weight of the resin combination. Those skilled in the art will be able to determine, without undue experimentation, any variation in the amount of HMW, VHMW and/or UHMW polyethylene resin to be added to the resin compositions in order to effect one or more of the aspects of the present invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples are illustrative of the compositions of the present invention. These are not intended to limit the invention in any manner.

An initial, three series of polyphenylene ether resin/high impact polystyrene resin compositions were formulated including zero, 0.75, 1.50, 3.00 and 6.00 phr of a polyethylene resin modifier.

In Series I, the formulations were modified with linear low density polyethylene (LLDPE) of Union Carbide, given the designation GRSN8320, and having a weight-average molecular weight of about 45,000.

In Series II, the formulations were modified with "ULTRAC®" VHMW polyethylene resin, supplied by Allied-Signal Corporation.

In Series III, the formulations were modified with "1900 UMHWTM" polyethylene resin, supplied by Himont Chemical Company, Inc.

The compositions of the formulations are given in Tables 1-3 below. All samples were compounded on a 30 mm Werner-Pfleiderer twin-screw extruder. Test specimens were injection molded on a 75 ton Newbury reciprocating screw machine with a 500° F. barrel temperature profile and a 150° mold temperature. Mechanical and flame retardancy tests were carried out in accordance with appropriate ASTM or UL procedures.

TABLE 1

COMPONENT	SERIES I LLDPE SAMPLE FORMULATIONS (parts by weight)				
	1	2	3	4	5
POLYPHENYLENE ETHER	60	60	60	60	60
HIGH IMPACT POLYSTYRENE	37	37	37	37	37
TRIPHENYL PHOSPHATE	18	18	18	18	18
TRIDECYLPHOSPHITE	0.5	0.5	0.5	0.5	0.5
ZnO	0.15	0.15	0.15	0.15	0.15
ZnS	0.15	0.15	0.15	0.15	0.15
LLDPE ( $M_w = 4.5 \times 10^4$ )	0.0	0.75	1.50	3.00	6.00

TABLE 2

COMPONENT	SERIES II "ULTRAC @" VHMWPE SAMPLE FORMULATIONS (parts by weight)			
	6	7	8	9
POLYPHENYLENE ETHER	60	60	60	60
HIGH IMPACT POLYSTYRENE	37	37	37	37
TRIPHENYL PHOSPHATE	18	18	18	18
TRIDECYLPHOSPHITE	0.5	0.5	0.5	0.5
ZnO	0.15	0.15	0.15	0.15
ZnS	0.15	0.15	0.15	0.15
ULTRAC @ VHMW ( $M_w = 2.0 - 3.0 \times 10^6$ )	0.75	1.50	3.00	6.00
POLYETHYLENE				

TABLE 3

COMPONENT	SERIES III HIMONT 1900 UHMWPE SAMPLE FORMULATIONS (Parts by weight)			
	10	11	12	13
POLYPHENYLENE ETHER	60	60	60	60
HIGH IMPACT POLYSTYRENE	37	37	37	37
TRIPHENYL PHOSPHATE	18	18	18	18
TRIDECYLPHOSPHITE	0.5	0.5	0.5	0.5
ZnO	0.15	0.15	0.15	0.15
ZnS	0.15	0.15	0.15	0.15
1900 UHMW TM ( $M_w = 3.0 - 6.0 \times 10^6$ )	0.75	1.50	3.00	6.00

The mechanical properties and flammability characteristics of the samples in Series I, II and III are given in Tables 4 and 5.

The effects of polyethylene modification on mechanical

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for predetermined period. Successively, supernatant is removed, and the resulting solid component is re-suspended in the inert hydrocarbon. Into the system, the transition metal compound (component (a)) is added and reacted for predetermined period. Then, supernatant is removed to obtain a solid catalyst component. Continuously, the solid catalyst component obtained above is added into inert hydrocarbon containing the organoaluminum compound (component (d)), and olefin is introduced therein to obtain the prepolymerized catalyst.

An amount of prepolymerized polyolefin produced in the prepolymerization is, desirably based on 1 g of the carrier (c), of 0.1 to 500 g, preferably 0.2 to 300 g, more preferably 0.5 to 200 g. In the prepolymerized catalyst, component (a) is desirably supported in an amount in terms of transition metal atom, based on 1 g of the carrier (c), of about  $5 \times 10^{-6}$  to  $5 \times 10^{-4}$  g atom, preferably  $1 \times 10^{-5}$  to  $1 \times 10^{-4}$  g atom. Further, a molecular ratio (Al/M) of aluminum atom (Al) derived from components (b) and (d) to transition metal atom (M) derived from component (a) is usually 5 to 200, preferably 10 to 150.

The prepolymerization may be carried out either batch-wise or continuously, and under reduced pressure, normal pressure or applied pressure. Though a molecular weight modifier such as hydrogen may be allowed to be present during prepolymerization, its amount is desirably restricted so that there can be prepared a prepolymer having an intrinsic viscosity  $[\eta]$  of 0.2 to 7 dl/g, preferably 0.5 to 10 dl/g as measured in decalin at 135°C.

The ethylene/α-olefin copolymers according to the present invention are obtained by copolymerizing ethylene with such an α-olefin having 3 to 20 carbon atoms as propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene.

In the present invention, olefin is usually polymerized in a gas phase or liquid phase, for example, in slurry. In the slurry polymerization, an inactive hydrocarbon or the olefin itself may be used as a solvent.

Concrete examples of the hydrocarbon solvent include aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane; aromatic hydrocarbons such as benzene, toluene and xylene; and petroleum fractions such as gasoline, kerosene and gas oil. Of these hydrocarbons, preferred are aliphatic hydrocarbons, alicyclic hydrocarbons and petroleum fractions.

In the present invention, the slurry polymerization is conducted at a temperature of usually -50° to 100°C., preferably 0° to 90°C.

In the present invention, the gas phase polymerization is carried out at a temperature of usually 0° to 120°C., preferably 20° to 100°C.

In the slurry polymerization or gas phase polymerization of the invention, the concentration of the transition metal compound is usually  $10^{-8}$  to  $10^{-3}$  g atom/liter, preferably  $10^{-7}$  to  $10^{-4}$  g atom/liter in terms of the transition metal.

Furthermore, in the polymerization of the invention, an aluminum oxy-compound or an aluminum compound similar to those used in the catalyst components (b) and (d) may be added. During the polymerization, the ratio of the aluminum compound in terms of Al atom to the transition metal atom (M) (Al/M) is 5 to 300, preferably 10 to 200, more preferably 15 to 150.

The polymerization is carried out usually at a normal pressure to 100 kg/cm<sup>2</sup>, preferably under a pressure condi-

tion of 2 to 50 kg/cm<sup>2</sup>. The polymerization can be carried out either batchwise, semicontinuously or continuously.

Furthermore, the polymerization may also be carried out in not less than 2 steps having reaction conditions different from each other.

The ethylene/α-olefin copolymer of the present invention can be used for films obtained by extrusion molding, pipes and tubes obtained by extrusion molding, fibers, containers obtained by blow molding, daily use miscellaneous goods obtained by injection molding, caps, and large-sized molded products obtained by rotational molding. Of these uses, the ethylene/α-olefin copolymer of the invention is suitable for films obtained by extrusion film molding, namely, inflation molding and T-die molding. Particularly, the ethylene/α-olefin copolymer of the invention is very suitable as resin for inflation molded films among the extrusion molded films. The inflation molded films are used for, for example, standard bags, heavy duty bags, wrapping films, materials for laminates, sugar bags, packaging bags for oily goods, packaging bags for moist goods, various packaging films for foods, agricultural materials and bags for liquid transportation. Further, the inflation molded films may also be used as multi-layer films by laminating the films on various substrates such as a nylon substrate and a polyester substrate.

The ethylene/α-olefin copolymer according to the invention may optionally contain various additives such as a weathering stabilizer, a heat stabilizer, an antistatic agent, an antislip agent, an antiblocking agent, an antioxidant agent, a lubricant, a pigment, a dye, a nucleating agent, a plasticizer, an age resistor, a hydrochloric acid absorbing agent, and an antioxidant, so long as the additives do not have an adverse effect. Further, some other high molecular compounds can be blended in a small amount within the spirit and scope of the invention.

The ethylene/α-olefin copolymer of the present invention is excellent in balance of melt tension and flowability, compared with conventional intermediate- or low-pressure ethylene copolymer. Therefore, the ethylene/α-olefin copolymer of the present invention shows considerably improved moldability during the extrusion molding. Further, the extrusion molded articles are excellent in transparency, impact strength, heat sealability and blocking property. Furthermore, the injection molded articles are excellent in strength properties such as impact strength and environmental stress resistance. The injection molded articles are also excellent in low-temperature properties.

The present invention is illustrated below with reference to examples, but it should be construed that the present invention is in no way limited to those examples.

Definition of physical properties of the ethylene/α-olefin copolymer, measuring methods of the physical properties and molding process of the ethylene/α-olefin copolymer, used in the invention, are described below.

#### (1) Granulation of ethylene/α-olefin copolymer

To a powdery ethylene copolymer obtained by gas phase polymerization were added 0.05% by weight of tri(2,4-di-t-butylphenyl)phosphate as a secondary antioxidant, 0.1% by weight of n-octadecyl-3-(4'-hydroxy-3',5'-di-t-butylphenyl)propionate as a heat-resistant stabilizer and 0.05% by weight of calcium stearate as a hydrochloric acid absorbing agent, each based on the amount (part(s) by weight) of the ethylene copolymer. Then, the resultant mixture was melt-extruded at a preset temperature of 180°C. using a conical-tapered twin-screw extruder (produced by Herque Co.), to prepare granulated pellets.

#### (2) Density

A strand of the copolymer obtained in MFR measurement at 190°C. under a load of 2.16 kg was heated at 120°C. over